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53/94				101Z
G05D 21/00			B01D 53/36	101A

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[Title of invention] Flue gas de-NOx-ing process and apparatus

[Abstract]
[Aim] To provide a flue gas de-NOx-ing process whereby the percentage NOx reduction can be easily and precisely controlled.
[Constitution] A flue gas de-NOx-ing process wherein an oxidant (O_3, H_2O_2, HNO_3, etc.) and NH_3 are injected into flue gas containing most of the NOx as NO, thereby converting part of the NO to NO_2, and the flue gas is then brought into contact with a de-NOx-ing catalyst 3 to remove the NOx in the flue gas by reduction; wherein the NH_3 injection rate required is computed by a processor 14 from information on flue gas flow rate 13 and information on flue gas NOx concentration 12 and the amounts of NH_3 and oxidant injected are controlled in tandem to a predefined ratio.

[Diagram: see Drawings, Fig.2]

[Scope of Claims]

[Claim 1] A flue gas de-NOx-ing process characterised as a flue gas de-NOx-ing process for the reductive removal of nitrogen oxides in flue gas containing most of the nitrogen oxides as nitric oxide (NO) by injecting an oxidant and ammonia into the flue gas to convert part of the nitric oxide to nitrogen dioxide (NO_2) and then bringing the flue gas into contact with a de-NOx-ing catalyst; wherein the ammonia injection rate required is computed from information on flue gas flow rate and information on the NOx concentration in the flue gas and the amounts of ammonia and oxidant injected are controlled in tandem to a predefined ratio.

[Claim 2] The flue gas de-NOx-ing process of Claim 1 characterised in that ozone or hydrogen peroxide is used as the oxidant and the molar ratio of amount of ammonia injected/ amount of oxidant injected is controlled to the range 2.0 ± 0.2 moi/mol.

[Claim 3] The flue gas de-NOx-ing process of Claim 1 characterised in that nitric acid is used as the oxidant and the molar ratio of the amount of ammonia injected/ amount of oxidant injected is controlled to the range 3.0 ± 0.3 mol/mol.

[Claim 4] Flue gas de-NOx-ing apparatus characterised as flue gas de-NOx-ing apparatus possessing means of injecting ammonia and an oxidant into flue gas containing nitric oxide and converting part of the nitric oxide to nitrogen dioxide, and a means of reductively removing nitrogen oxides by effecting contact of the converted flue gas with a de-NOx-ing catalyst; wherein is provided a means of interlocking the aforesaid ammonia and oxidant injection rate control means and controlling the molar ratio of ammonia injected/oxidant injected to a predefined ratio.

[Claim 5] The flue gas de-NOx-ing apparatus of Claim 4 characterised in that the oxidant is ozone or hydrogen peroxide and a means is provided for controlling the molar ratio of amount of ammonia injected/ amount of oxidant injected to the range 2.0 ± 0.2 mol/mol.

[Claim 6] The flue gas de-NOx-ing apparatus of Claim 4 characterised in that oxidant is nitric acid and a means is provided for controlling the molar ratio of the amount of ammonia injected/ amount of oxidant injected to the range 3.0 ± 0.3 mol/mol.

[Detailed Description of Invention]

[0001]
[Field of industrial utility] The invention relates to a flue gas de-NOx-ing process and apparatus, and in particular relates to a flue gas de-NOx-ing process and apparatus whereby the nitrogen oxides (NOx) in the flue gas discharged from power plant boilers, gas turbines and various

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combustion furnaces such as refuse incinerators can be catalytically reduced with ammonia (NH_3) at low temperature and good efficiency by virtue of prior oxidation of part of the nitric oxide (NO) in the nitrogen oxides to nitrogen dioxide (NO_2).
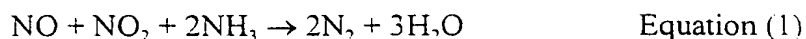
[0002]
[Prior art] In catalytic reductive de-NOx-ing with ammonia, wherein the nitrogen oxides in flue gas are reduced to nitrogen by injection of ammonia (NH_3) into the flue gas followed by contact with a catalyst, numerous examples are known of attempts to improve reactivity with NH_3 so that de-NOx-ing can be effected at a lower temperature by the injection of an oxidant into the flue gas to convert part of the nitric oxide (NO) to nitrogen dioxide (NO_2) beforehand (for instance Japan Patent Kokai No.52-94863, Japan Patent publication No.56-50613 and Japan Patent Kokai No.54-23068).

[0003] Since the reaction of 1 mole of nitric oxide and 1 mole of nitrogen dioxide with 2 moles of NH_3 shown in Equation (1) is extremely fast compared with the conventional de-NOx-ing reaction shown in Equation (2), the aforesaid processes seek to reduce the operating temperature by either injecting a nitrogen dioxide source or injecting an oxidant such as ozone (O_3), hydrogen peroxide (H_2O_2) or nitric acid (HNO_3) to oxidise part of the NO to NO_2 beforehand (Equations (3)-(5)).
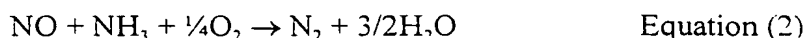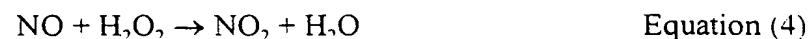
[0004]
[Formulae/1]

$$NO + NO_2 + 2NH_3 \rightarrow 2N_2 + 3H_2O \qquad \text{Equation (1)}$$

[0005]
[Formulae/2]

$$NO + NH_3 + \tfrac{1}{4}O_2 \rightarrow N_2 + 3/2H_2O \qquad \text{Equation (2)}$$

[0006]
[Formulae/3]

$$NO + O_3 \rightarrow NO_2 + O_2 \qquad \text{Equation (3)}$$

[0007]
[Formulae/4]

$$NO + H_2O_2 \rightarrow NO_2 + H_2O \qquad \text{Equation (4)}$$

[0008]
[Formulae/5]

$$NO + 2HNO_3 \rightarrow 3NO_2 + H_2O \qquad \text{Equation (5)}$$

Since the aforesaid benefit of having both NO and NO_2 present is prominent at 100-300°C, attempts have long been made to apply the art to low temperature de-NOx-ing in flue gas from various incinerators, waste heat recovery boilers, and combustors such as gas turbines. However, the art has still not found wide practical application.

[0009]

[Problem addressed by invention] The prime reason why practical application of the aforesaid prior art has been hindered may be identified as the difficulty of controlling the percentage NOx reduction. Fig.5 shows the temperature characteristic in the de-NOx-ing of various flue gases containing NO alone, NO_2 alone and equimolar NO plus NO_2 using a titanium (Ti)-tungsten (W)-vanadium (V) catalyst. Whereas NOx is efficiently removed when NO and NO_2 are present in equimolar amounts, de-NOx-ing performance declines greatly for NO or NO_2 alone. The prior art for individually controlling the rate of injection of oxidant and rate of injection of NH_3 in response to variation in NOx content therefore creates many problems such as the following.

(A) When there is an oxidant deficit and the proportion of NO_2 contained in the flue gas is small, the rate of the de-NOx-ing reaction decreases and efflux of a large amount of unreacted ammonia occurs.

(B) When the NO_2 concentration in the flue gas exceeds the NO concentration, the de-NOx-ing reaction switches to reaction of 4 moles of ammonia with 3 moles of nitrogen dioxide (Equation (6)), making it difficult to control the amount of NH_3 injected. Furthermore, when the NO_2 concentration exceeds the NO concentration, ammonium nitrate is formed from the NO_2 and NH_3 with the result that the catalyst slowly deteriorates and N_2O is formed as a by-product.

[0010]
[Formulae/6]

$$3NO_2 + 4NH_3 \rightarrow 7/2N_2 + 6H_2O \qquad \text{Equation (6)}$$

(C) Unless the NH_3 injected matches the NO_2 content, the oxide NO_2, which pollutes more readily than NO, is discharged from the stack and the vent gas turns yellow.

In view of such problems with the prior art, the present invention seeks to provide de-NOx-ing apparatus, similar to the widely deployed ammonia catalytic reduction process de-NOx-ing apparatus for flue gas addressed primarily to NO, whereby the percentage NOx reduction can be easily and precisely controlled, while also providing a de-NOx-ing process that does not create the aforementioned problems.

[0011]
[Means of solving the problems] To achieve the aforesaid aim, the invention claimed for this Patent Application is constituted as follows.

(1) A flue gas de-NOx-ing process characterised as a flue gas de-NOx-ing process for the reductive removal of nitrogen oxides in flue gas containing most of the nitrogen oxides as nitric

oxide (NO) by injecting an oxidant and ammonia into the flue gas to convert part of the nitric oxide to nitrogen dioxide (NO_2) and then bringing the flue gas into contact with a de-NOx-ing catalyst; wherein the ammonia injection rate required is computed from information on flue gas flow rate and information on the NOx concentration in the flue gas and the rates of injection of ammonia and oxidant are controlled in tandem to a predefined ratio.

(2) The flue gas de-NOx-ing process of (1) characterised in that ozone or hydrogen peroxide is used as the oxidant and the molar ratio of amount of ammonia injected/ amount of oxidant injected is controlled to the range 2.0±0.2 mol/mol.

(3) The flue gas de-NOx-ing process of (1) characterised in that nitric acid is used as the oxidant and the molar ratio of the amount of ammonia injected/amount of oxidant injected is controlled to the range 3.0±0.3 mol/mol.

(4) Flue gas de-NOx-ing apparatus characterised as flue gas de-NOx-ing apparatus possessing means of injecting ammonia and an oxidant into flue gas containing nitric oxide and converting part of the nitric oxide to nitrogen dioxide, and a means of reductively removing nitrogen oxides by effecting contact of the converted flue gas with a de-NOx-ing catalyst; wherein is provided a means of interlocking the aforesaid ammonia and oxidant injection rate control means and controlling the molar ratio of amount of ammonia injected/amount of oxidant injected to a predefined ratio.

(5) The flue gas de-NOx-ing apparatus of (4) characterised in that the oxidant is ozone or hydrogen peroxide and a means is provided for controlling the molar ratio of amount of ammonia injected/amount of oxidant injected to the range 2.0±0.2 mol/mol.
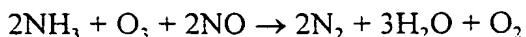
(6) The flue gas de-NOx-ing apparatus of (4) characterised in that oxidant is nitric acid and a means is provided for controlling the molar ratio of the amount of ammonia injected/amount of oxidant injected to the range 3.0±0.3 mol/mol.

[0012]
[Action and effect] The aforementioned reaction of Equation (1) is extremely rapid when the rates of injection of NH_3 and oxidant are controlled within the aforementioned range as in the invention; the oxidant and NH_3 are therefore rapidly consumed without excess or deficit by the overall reactions of Equations (7)-(9) shown hereunder.

[0013]
[Formulae/7]

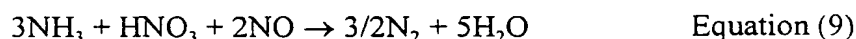$$2NH_3 + O_3 + 2NO \rightarrow 2N_2 + 3H_2O + O_2 \qquad \text{Equation (7)}$$

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[0014]
[Formulae/8]

$$2NH_3 + H_2O_2 + 2NO \rightarrow 2N_2 + 4H_2O \qquad \text{Equation (8)}$$

[0015]
[Formulae/9]

$$3NH_3 + HNO_3 + 2NO \rightarrow 3/2N_2 + 5H_2O \qquad \text{Equation (9)}$$

Hence, the problems in the prior art that occur when either the NO or NO_2 concentration of the flue gas is preponderant, namely a decreased percentage NOx reduction, leakage of NO_2, formation of N_2O by-product or catalyst deterioration, cannot arise in the invention. Even if more NH_3 and oxidant than necessary to remove the NO from the flue gas were to be injected, only NH_3 and harmless oxygen would leak in the case of O_3 and H_2O_2 injection, as in conventional flue de-NOx-ing apparatus. Although NO_2 would leak when the oxidant is HNO_3, the amount leaked would be extremely small since the amount injected is no more than a third of the amount of NH_3 injected, and the consequences thereof would be far less serious.

[0016] Accordingly, the de-NOx-ing activity in operation of the process can be set by varying the rate of ammonia injection without reference to the oxidation reaction. Furthermore, since the rapid reaction of Equation (7), (8) or (9) can be effected exclusively at all times, it is possible to reduce the amount of catalyst used or use a lower reaction temperature. By controlling the amount of ammonia injected and amount of oxidant injected to a fixed ratio at all times as indicated, it is possible to operate the apparatus with the same ease as for the de-NOx-ing apparatus currently in general use.

[0017] The means adopted in the invention is characterised by being so constituted that information on the NOx concentration in the flue gas can be obtained and the NO oxidant and NH_3 added in a fixed ratio according to the said concentration signal.

[0018]
[Working Example] Fig.1 shows the basic flow sheet of the flue gas de-NOx-ing apparatus in a working example of the invention. The de-NOx-ing apparatus consists of NOx concentration measuring apparatus 9, oxidant injection apparatus 10, NH_3 injection apparatus 11, and a catalytic reactor 2; wherein the oxidant injection apparatus 10 and the NH_3 injection apparatus 11 are controlled according to the concentration signal 12 from the NOx measurement apparatus 9 and the flow rate signal 13 so that the amounts injected maintain a predefined, fixed molar ratio at all times.

[0019] The fixed molar ratio of the amounts of oxidant and NH_3 injected here signifies a ratio in the following ranges according to the species of oxidant.

(A) When the oxidant is O_3 or H_2O_2:
amount of NH_3 injected/amount of oxidant injected = 2.0±0.2 mol/mol
(B) When the oxidant is HNO_3:
amount of NH_3 injected/amount of oxidant injected = 3.0±0.3 mol/mol.

In addition to a means of injecting oxidant into the flue gas such as an ozone generator or hydrogen peroxide or nitric acid aspirator, the oxidant injection apparatus 10 includes the control means associated therewith, e.g. control valves for controlling the flow of oxidant from the generator and the means of controlling the rate of ozone generation by controlling the voltage applied to the discharge generator.

[0020] The basic composition of the apparatus required for practising the invention is shown in Fig.1. The de-NOx-ing apparatus comprises NOx concentration measuring apparatus 9, oxidant injection apparatus 10, NH_3 injection apparatus 11, and a catalytic reactor 2, and is so constituted that the oxidant injection apparatus 10 and the NH_3 injection apparatus 11 are controlled by the concentration signal 12 from the NOx measurement apparatus 9 and the flow rate signal 13 to give a predefined, fixed molar ratio between the amounts of oxidant and ammonia injected at all times.
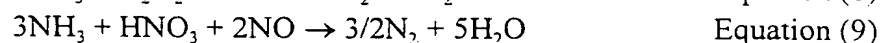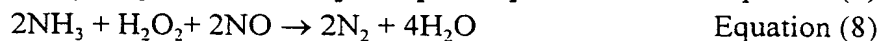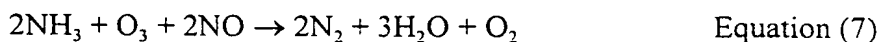
[0021] A conventional NOx concentration measuring apparatus such as infrared or chemiluminescence apparatus is used for the NOx concentration measuring apparatus 9, which generates a signal proportional to the NOx concentration in the flue gas. The flow rate signal 13, on the other hand, may be obtained from the flue gas source, and may be generated by independent metering with a Pitot tube, orifice plate or the like. The two signals are sent to the oxidant injection apparatus 10 and ammonia injection apparatus 11 and converted to injection rate control signals which are used to control the injection rates of the two reactants so that the injection rates follow the changes in gas flow rate and NOx concentration and the amount of ammonia injected/amount of oxidant injected assumes a fixed molar ratio at all times. As hereinbefore noted, the point of the invention is to control the rates of injection so that the amount of ammonia injected/amount of oxidant injected assumes a fixed molar ratio at all times; clearly, therefore, a control signal 15 whereby the amount of ammonia injected/amount of oxidant injected assumes a fixed molar ratio at all times may be generated by pre-processing the flow rate signal 13 and NOx concentration signal 12 with a processor 14 as in Fig.2.

[0022] The ammonia injection apparatus 11 comprises apparatus for feeding ammonia, for example ammonia gas or liquefied ammonia, and a control means such as a flow control valve, and supplies ammonia in an amount proportional to the aforesaid control signal. The same applies to the oxidant injection apparatus, the difference being that injection is controlled in tandem with the ammonia injection rate so that the molar ratio of amount of ammonia injected/amount of oxidant injected is fixed at all times.

[0023] An oxidant with the ability to oxidise the NO in flue gas to NO_2, for example ozone, nitric acid or hydrogen peroxide, is used in the invention, the rate of injection being controlled to give the molar ratio of amount of ammonia injected/amount of oxidant injected set down in the Claims according to the species of oxidant. The catalyst 3 herein used is a conventional de-NOx-ing catalyst such as the known titanium oxide based catalysts and zeolitic catalysts.

[0024] After part of the NO has been oxidised to NO_2 by the oxidant injected into the flue gas as in the aforesaid Equations (3)-(5), ammonia is added and the gas is admitted to the catalytic reactor; wherein, since the ammonia and oxidant are controlled so that the molar ratio of amount of ammonia injected/amount of oxidant injected is fixed at all times, the very rapid reaction of Equation (7), (8) or (9) proceeds selectively and the ammonia and oxidant are consumed without excess or deficit.

[0025]

$$2NH_3 + O_3 + 2NO \rightarrow 2N_2 + 3H_2O + O_2 \qquad \text{Equation (7)}$$
$$2NH_3 + H_2O_2 + 2NO \rightarrow 2N_2 + 4H_2O \qquad \text{Equation (8)}$$
$$3NH_3 + HNO_3 + 2NO \rightarrow 3/2N_2 + 5H_2O \qquad \text{Equation (9)}$$

Since a very rapid selective reaction is thus effected, the operating temperature can be greatly reduced, a great saving in the amount of catalyst being secured by operation at 100-300°C. normally 150-250°C. Moreover, as already noted, there is almost no efflux of unreacted ammonia or formation of NO_2 by the oxidant, eliminating the various problems of concern in the prior art.

[0026] Although de-NOx-ing can be conducted most efficiently when the molar ratio of amount of ammonia injected/amount of oxidant injected is set at 2 when O_3 or H_2O_2 is used and at 3 when HNO_3 is used, an efficiency high enough for practical purposes is obtained without problems arising if the ratio is within the range set down in the Claims. A molar ratio greater or smaller than the aforesaid range is undesirable in that it results in a decrease in the percentage NOx reduction, deterioration of the catalyst or formation of N_2O by-product.

[0027] Moreover, although the molar ratio of NH_3 injected to the NO in the flue gas is preferably controlled to not more than 1 in the case of H_2O_2 and not more than 1.5 in the case of HNO_3, the ratio may be varied accordingly when the flue gas contains NO_2 to begin with. Although the invention affords a particularly marked benefit at low temperature, the apparatus may also have a facility that retains heat in the flue gas for reasons such as protecting the apparatus from corrosion. The benefit in reducing the amount of catalyst is also obtained when the method of controlling the ratio of amount of ammonia injected/amount of oxidant injected to a fixed value consonant with the principle of the invention is adopted at irregular intervals as a method of cleaning up low temperature flue gas in the start up of gas turbines.

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[0028] The principle of the invention is not confined to the arrangements indicated in Fig.1 and Fig.2: similar benefits are obtained with apparatus wherein, if necessary, other flue gas clean-up equipment or waste heat apparatus has been incorporated, or whereto such changes have been made as locating the ammonia injection in the high temperature zone at the combustor exit; such arrangements are encompassed by the invention. Fig.3 shows an example where dust collector apparatus 16 has been provided between the combustor 1 and catalytic reactor 2, as appropriate to the treatment of flue gas of high soot and dust content such as refuse incinerator flue gas. Furthermore, Fig.4 shows an example incorporating a heat-exchanger or heat recovery unit 17 in the flue gas line, the arrangement being designed to accelerate oxidation of NO by oxidant by injection of the oxidant upstream of the heat recovery unit 17 or in the heat recovery heating tube bank. Note that although the working examples in Figs.1-4 illustrate the case where ammonia is injected downstream after injection of the oxidant, it is permissible to inject the ammonia and oxidant simultaneously at the same point since rapid oxidation of nitric oxide to nitrogen dioxide by the oxidant is achieved.

[0029] Specific data from working examples of the invention are described in further detail hereunder in comparison with data for existing de-NOx-ing apparatus.

Working Example 1

A gas with the composition in Table 1 was passed into a miniature reaction apparatus embodying the system of Fig.1 and de-NOx-ing was performed. The oxidant used was gas of 1000 ppm O_3 concentration generated from an ozone generator, while 2% ammonia gas was used as the de-NOx-ing reductant; the gas lines were connected to respective flow rate control valves and the two signals were interlocked to give an NH_3/O_3 molar ratio of 2 at all times. The de-NOx-ing reactor used was a catalyst structure wherein Ti-W-V catalyst (Ti/W/V atomic ratio = 95/4/5, thickness 1 mm) in sheet form was arranged at a pitch of 4 mm, and was maintained under the conditions shown in Table 2.

[Table 1]

NO	200 ppm
CO_2	6%
O_2	10%
H_2O	6%
N_2	remainder

[0031]
[Table 2]

gas flow rate	0.2 m³/h
areal velocity	17 m/h
reaction temperature	150°C

The NH_3/NO ratio was varied between 0.4 and 1.4 mol/mol under these conditions; the percentage decrease in NOx and the concentration of N_2O at the catalyst bed exit were measured and the change in vent gas colour was examined.

Comparative Example 1 and Comparative Example 2

Using the same apparatus as in Working Example 1, de-NOx-ing was carried out as in Working Example 1 except that ozone was injected at a constant rate to give O_3/NO molar ratios of 0.4 and 0.6. The NH_3/NO ratio was again varied between 0.4 and 1.4 mol/mol; the percentage decrease in NOx and the concentration of N_2O at the catalyst bed exit were measured and the change in vent gas colour was examined.

[0032] The results obtained from Working Example 1 and Comparative Examples 1 and 2 are compared in Table 3.

[0033]

[Table 3]

	NH$_3$/NO ratio (mol/mol)	NOx reduction (%)	N$_2$O by-product (ppm)	vent gas colour	remarks
Working Example 1	0.4	40.5	0.0	colourless	
	0.6	59.3	0.0	"	
	0.8	78.6	0.0	"	
	1.0	93.4	0.0	"	
	1.2	95.7	0.1	"	
	1.4	97.6	0.0	"	
Comparative Example 1	0.4	41.3	1.5	yellow	
	0.6	59.1	0.3	pale yellow	
	0.8	79.2	0.0	colourless	
	1.0	76.2	6.2	"	
	1.2	81.4	13.4	"	
	1.4	83.3	17.2	"	
Comparative Example 2	0.4	43.0	8.1	brown	
	0.6	60.2	7.3	"	
	0.8	80.6	9.6	yellow	
	1.0	83.1	14.5	"	
	1.2	85.3	17.2	"	} white precipitate on reactor
	1.4	88.3	17.6	"	} tube wall

A percentage NOx reduction consistent with the NH$_3$/NO molar ratio was obtained in Working Example 1, a high efficiency being obtained at an NH$_3$/NO ratio above 0.8. Moreover, no N$_2$O by-product formed and there was no change in vent gas colour at any NH$_3$/NO ratio.

[0034] In Comparative Example 1, on the other hand, the percentage NOx reduction never went above a certain level; moreover, N$_2$O by-product formed and the vent gas turned yellow when the NH$_3$/NO ratio was small. Comparative Example 2 similarly failed to afford a high percentage NOx reduction, and the formation of N$_2$O and discoloration of the flue gas were seen at all NH$_3$/NO ratios. Furthermore, a phenomenon was observed whereby the de-NOx-ing performance gradually declined when the process was held at a high NH$_3$/NO ratio for an extended period.

Working Example 2

Instead of the ozone generator and flow rate control valve of Working Example 1, 15% nitric acid was injected as oxidant using a constant delivery pump of controllable flow rate and an externally heated vaporiser provided at the exit thereof, and the molar ratio of NH$_3$/HNO$_3$ injected was controlled to 3 at all times. Apart from use of the said apparatus, de-NOx-ing was conducted as in Working Example 1, and the percentage decrease in NOx and the concentration

of N_2O at the catalyst bed exit were measured and the change in vent gas colour was examined when the NH_3/NO ratio was varied between 0.4 and 1.4 mol/mol.

Comparative Example 3 and Comparative Example 4

Using the same apparatus as in Working Example 2, de-NOx-ing was carried out as in Working Example 2 except that the aqueous nitric acid solution was injected at a constant rate to give HNO_3/NO molar ratios of 0.2 and 1.0. The NH_3/NO ratio was again varied between 0.4 and 1.4 mol/mol; the percentage decrease in NOx and the concentration of N_2O at the catalyst bed exit were measured and the change in vent gas colour was examined.

[0035] The results from Working Example 2 and Comparative Examples 3 and 4 are shown together in Table 4.

[0036]
[Table 4]

	NH_3/NO ratio (mol/mol)	NOx reduction (%)	N_2O by-product (ppm)	vent gas colour	remarks
Working Example 2	0.4	39.2	0.1	colourless	
	0.6	58.8	0.2	"	
	0.8	79.2	0.4	"	
	1.0	93.1	0.1	"	
	1.2	94.6	0.3	"	
	1.4	95.3	0.4	"	
Comparative Example 3	0.4	41.3	1.1	pale yellow	
	0.6	59.1	0.2	colourless	
	0.8	79.2	0.7	"	
	1.0	76.2	0.9	"	
	1.2	81.4	1.8	"	
	1.4	83.3	2.5	"	
Comparative Example 4	0.4	24.6	12.1	brown	} white precipitate on reactor tube wall
	0.6	37.6	7.3	"	
	0.8	48.6	9.6	"	"
	1.0	51.2	14.5	"	"
	1.2	53.2	17.2	"	"
	1.4	42.0	17.6	"	"

A high percentage NOx reduction similar to that in Working Example 1 was obtained in Working Example 2; moreover, neither the formation of N_2O by-product nor discoloration of the flue gas was seen.

[0037] In contrast, a high percentage NOx reduction was unobtainable in Comparative Examples 3 and 4; moreover, the formation of N_2O by-product and strong yellow discoloration of the flue gas were noted. Furthermore, it was found that ammonium sulphate precipitated on the reactor tube wall at high NH_3/NO ratios, creating a serious problem for practical application.

Working Example 3

Instead of the ozone generator and flow rate control valve of Working Example 1, aqueous 10% hydrogen peroxide was injected as oxidant using a constant delivery pump of controllable flow rate and an externally heated vaporiser provided at the exit thereof, and the molar ratio of NH_3/H_2O_2 injected was controlled to 2 at all times. Apart from use of the said apparatus, de-NOx-ing was conducted as in Working Example 1 and the percentage decrease in NOx and the concentration of N_2O at the catalyst bed exit were measured and the change in vent gas colour was examined when the NH_3/NO ratio was varied between 0.4 and 1.4 mol/mol. As in Working Examples 1 and 2, a high percentage NOx reduction was obtained; moreover, the process exhibited excellent characteristics, with no sign of the N_2O formation and flue gas discoloration that pose problems in the operation of de-NOx-ing apparatus.

[0038]
[Benefit of invention] The invention enables the efficient de-NOx-ing of low temperature flue gas without creating the problems that hinder practical application, namely the formation of N_2O by-product and discoloration of the flue gas due to persistence of NO_2. Furthermore, since large variations in NH_3/NO molar ratio can be smoothly handled, load fluctuations and changes in NOx concentration are easily followed.

[0039] Since various low temperature flue gases including the flue gas from refuse incinerators for which demand has recently grown can thereby be efficiently processed without waste heat retention, the invention has very considerable industrial and social value.

[Brief Description of Drawings]

[Fig.1] A block diagram of de-NOx-ing apparatus showing a working example of the invention.
[Fig.2] A block diagram of de-NOx-ing apparatus showing another working example of the invention.
[Fig.3] A diagram illustrating another practical embodiment of the invention.
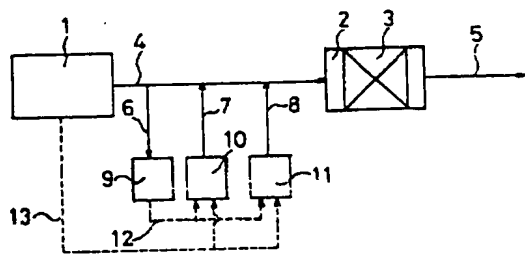[Fig.4] A diagram illustrating another practical embodiment of the invention.
[Fig.5] A diagram explaining the problems of the prior art.
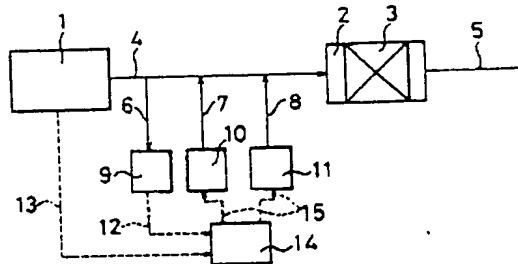
[Key to symbols]

1... flue gas source, 2... catalytic reactor, 3... catalyst, 4,5... exhaust pipes, 6... NO$_x$ sampling tube, 7... oxidant injection line, 8... ammonia injection line, 9... NO$_x$ concentration meter, 10... oxidant injection apparatus, 11... ammonia injection apparatus, 12... NO$_x$ concentration signal, 13... flow rate signal, 14... processor, 15... injection rate control signal
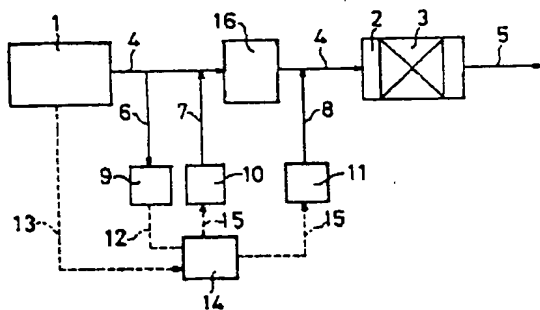
Fig.1

Fig.2

1 flue gas source (combustion furnace)
2 catalytic reactor
3 catalyst
4,5 exhaust pipes
6 NO$_x$ sampling tube
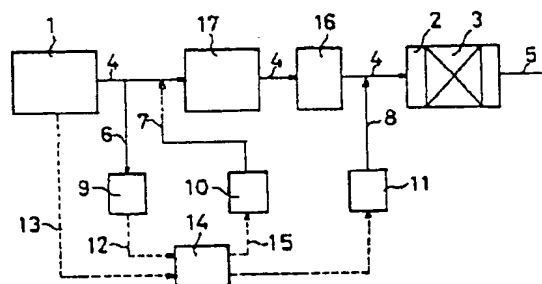7 oxidant injection line
8 ammonia injection line

9 NO$_x$ concentration meter
10 oxidant injection apparatus
11 ammonia injection apparatus
12 NO$_x$ concentration signal
13 flow rate signal
14 processor
15 injection rate control signal

Fig.3

Fig.4

1 flue gas source (combustion furnace)
2 catalytic reactor
3 catalyst
4,5 exhaust pipes
6 NO$_x$ sampling tube
7 oxidant injection line
8 ammonia injection line
9 NO$_x$ concentration meter

10 oxidant injection apparatus
11 ammonia injection apparatus
12 NO$_x$ concentration signal
13 flow rate signal
14 processor
15 injection rate control signal
16 dust separator
17 heat recovery unit (heat exchanger)

14

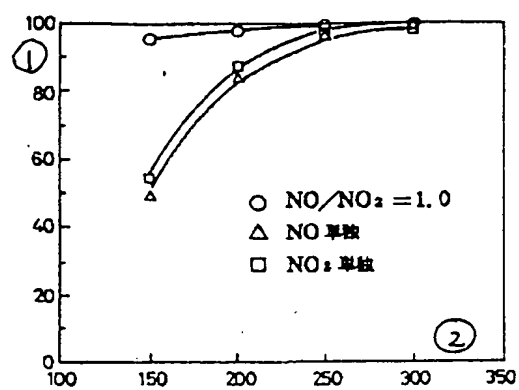**Fig.5**

(1) NOx removal (%)

(2) temperature (°C)

    O NO/NO$_2$ = 1.0

    △ NO alone

    □ NO$_2$ alone

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